XV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

THE ELECTROMOTIVE FORCE OF ALLOYS.

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THE best study of alloys and the most thorough work on them has been done by Matthiessen, who proved conclusively that alloys were neither mechanical mixtures nor chemical compounds, but what he terms, in a general way, "a solidified solution of one metal in another." He also showed that, with reference to the formation of alloys, metals were divided into two classes; — the first class being those which, when alloyed with each other, give a conductivity in proportion to the respective volumes of the two metals; and the second, those which, when alloyed with each other, give a conductivity which is less than that of the respective volumes of the two metals.

The aim of this investigation has been to note the variation of electromotive force in different alloys of the same metals, and to deduce, if possible, some general law which governs the variation.

Two sets of alloys were used, — one set of lead and tin, and the other of copper and zinc. The first set was made by taking the proportional weights of lead and tin and melting them together in a crucible, and then pouring them out on a flat surface and allowing them to cool. The second set was made by melting a weighed amount of copper in a Fletcher gas-furnace, and, when in a molten state, adding more than the required amount of zinc, in order to make allowance for volatilization. Pure metals were obtained, in order that the results might be as accurate as possible.

It was deemed sufficient, as far as the lead and tin alloys were concerned, to weigh out carefully the required amounts of each metal, and to take those weights as showing the composition. This could not be done with the copper and zinc alloys, as it is impossible to determine

how much of the zinc volatilizes; so with these it is necessary to resort to analytical methods of determining the per cent of each. The copper was determined by electrolysis, by precipitating the copper, from a sulphuric acid solution of the alloy, upon a platinum disk connected with the negative pole of a battery, and the positive pole dipping in the solution. The zinc was determined by subtracting the per cent of copper from a hundred per cent.

The composition of the alloys are given in the tables below, and will be referred to by number hereafter.

Number.	Alloys of Sn and Pb.		Number.	Alloys of Cu and Zn.	
	Parts by Weight of Sn.	Parts by Weight of Pb.		% of Cu.	% of Zn.
I.	1	9	I.	91.92	8.08
II.	2	8	II.	85.75	14.25
III.	3	7	III.	72.99	27.01
IV.	4	6			
V.	5	5	IV.	66.70	33.30
VI.	6	4	V.	49.32	50.68
VII.	7	3	VI.	27.99	72.01
VIII.	8	2			
IX.	9	1	VII.	7.53	92.47

Four determinations were made with these alloys, the first two being the observation of the electromotive force of each alloy, with platinum for the positive pole and the alloy as the negative pole, with Fresh Pond water as the liquid; the second two being the determination of the electromotive force with the same positive pole, but with distilled water acidulated with a small quantity of sulphuric acid for a liquid. A mirror galvanometer and ground-glass scale were used, and a large resistance placed in the circuit, and the galvanometer shunted so as to reduce the deflection.

The first two tables do not give any general law for the electromotive force of alloys, the force being especially irregular, which is perhaps due to the fact that the electromotive forces of the two metals are very nearly alike.

The explanation of the third table is rather unsatisfactory, since the sulphate of lead is insoluble, while the sulphate of tin is not known; and this last may account for the change from the first tables. In the fourth table, the increase in electromotive force of the alloys containing the more copper may be accounted for by the fact that the sulphate of copper is more readily soluble than the sulphate of zinc.

I. The electromotive force of the alloys of tin and lead, and of the metals themselves, when the resistance is 7,180 ohms, and the constant of the galvanometer .000003435.

The first column gives the deflection in millimeters; the second, the tangent of one half the angle of deflection; the third, the product of the constant by the total resistance; and the fourth, the electromotive force in volts. The liquid in this case is water.

Number.	Deflection.	Tan ½ Angle of Deflection.	E. M. F. in Volts.
Pb	207	.0953	0.238
I.	205	.0942	0.249
II.	182	.0837	0.222
III.	173	.0795	0.201
IV.	212	.0975	0.258
V.	184	.0846	0.224
VI.	216	.0993	0.263
VII.	175	.0805	0.213
VIII.	208	.0956	0.253
IX.	195	.0896	0.237
Sn	164	.0754	0.199

II. The electromotive force of the alloys of copper and zinc, with a total resistance of 19,708 ohms, the constant being the same as before, and the liquid Fresh Pond water.

Number.	Deflection.	Tan ½ Angle of Deflection.	E. M. F. in Volts.
Cu	10	.0046	0.031
I.	12	.0055	0.037
II.	17	.0078	0.053
III.	52	.0239	0.162
IV.	64	.0294	0.199
V.	106	.0487	0.330
VI.	131	.0602	0.408
VII.	218	.1002	0.678
Zn	228	.1048	0.709

The resistance of distilled water is so great, that it was impossible to get any good or satisfactory results. The addition of about one

tenth of a cubic centimeter of strong sulphuric acid to about one hundred and fifty cubic centimeters of distilled water, gave the liquid used in the last two observations.

III. The electromotive force of the alloys of lead and tin, with total resistance of 22,608 ohms, the constant being the same, and the liquid as stated above.

Number.	Deflection.	Tan ½ Angle of Deflection.	E. M. F. in Volts.
Pb	185	.0881	0.661
I.	193	.0887	0.689
II.	195	.0896	0.696
III.	198	.0911	0.708
IV.	197	.0906	0.704
V.	196	.0902	0.701
VI.	194	.0892	0.693
VII.	198	.0911	0.708
VIII.	189	.0874	0.679
IX.	104	.0892	0.693
Sn	202	.0929	0.722

IV. The electromotive force of the alloys of copper and zinc, with a total resistance of 2,380 ohms, and the same constant of galvanometer and the same liquid as in the preceding determination.

Number.	Deflection.	Tan ½ Angle of Deflection.	E. M. F. in Volts.
Cu	43	.0188	0.153
I.	34	.0156	0.130
II.	40	.0184	0.150
III.	43	.0188	0.153
IV.	47	.0216	0.176
V.	55	.0253	0.206
VI.	115	.0529	0.432
VII.	203	.0939	0.768
Zn	234	.1763	1.442

It would seem to follow, from the last table at least, that in acid solutions the electromotive force of alloys is determined by the proportional part of that metal which is most readily attacked by the acid.

The general differences in the behavior of the two sets of alloys may perhaps be accounted for by the distinction which Matthiessen* made between the two kinds of alloys. He classes an alloy of lead and tin among those which are "solidified solutions of one metal in another," while he calls alloys, like copper and zinc, "solidified solutions of one metal in an allotropic modification of another."

* British Association Report, 1863, p. 47.